ELASTOMERIC COMPOSITION USEFUL AS TYRE TREADS

The present invention relates to a partially epoxidated elastomeric composition useful for the preparation of tyre treads.

The use of elastomers in the formulation of compounds for tyres, requires the availability of vulcanized products characterized by a low hysteresis for reducing the consumption of fuel.

To obtain good adhesion on wet surfaces and a good abrasion resistance, it is also necessary for the above compounds to be characterized by a suitable hysteretic dissipation at very high frequency stress.

To solve this problem, numerous studies have been carried out on the use of silica as a filler. These studies have given good results in the presence of polar elastomers such as nitrile rubber or chloroprene, in whose presence vulcanized products are obtained characterized by good tensile properties and wear resistance.

On the contrary the use of silica for reinforcing only slightly polar elastomers such as styrene butadiene copolymers or polybutadiene, is hindered by the poor mechanical properties obtained with these elastomers.

Attempts have been made to overcome these drawbacks by using, in the compounding phase, particular organosilanes containing sulfur, the so-called mercaptosilanes (EP-A-447.066). This solution is difficult owing to the cost of these mercaptosilanes and has the disadvantage of the special precautions required for their handling, in situ modification and the vulcanization of the above compounds.

An elastomeric composition has now been found which can be used for the production of treads for tyres which overcomes the above disadvantages. In fact the preparation of the elastomeric composition of the present invention does not require particular mercaptosilanes.

In accordance with this, the present invention relates to an elastomeric composition vulcanizable with sulfur and/or sulfur donors useful for the preparation of tyre treads which comprises:

a) 100 parts of an elastomeric mixture comprising from 20 to 100% by weight, preferably from 40 to 100% by

weight, of an elastomer deriving from the polymerization of a monovinylarene with a conjugated diene, preferably a styrene-butadiene copolymer, the complement to 100 being selected from natural rubber, polybutadiene and other diolefin elastomers;

b) from 10 to 150, preferably from 10 to 80, even more preferably from 30 to 60, parts of silica per 100 parts of (a);

c) from 0 to 150, preferably from 2 to 50, even more preferably from 3 to 30, parts of carbon black per 100 parts of (a);

characterized in that the elastomeric mixture (a) has an epoxidation degree, defined by the number of moles of epoxidated double bonds with respect to the initial number of moles of diene double bonds, of between 0.7 and 8.0%, preferably between 1.5 and 6.0%.

The monovinylarene contains from 8 to 20 carbon atoms per molecule and can contain alkyl, cycloalkyl, aryl substituents. Examples of these monovinylarene monomers are: styrene, α-methylstyrene, 3-methylstyrene, 4-n-propylstyrene, 4-cyclohexylstyrene, 4-dodecylstyrene, 2-ethyl-4-benzylstyrene, 4-p-tolylstyrene, 4-(4-phenyl-n-butyl)styrene, 1-vinyl naphthalene, 2-vinyl naphthalene.

In the preferred embodiment styrene is the pre-

ferred monovinylarene.

Conjugated dienes useful for the preparation of the monovinylarene/conjugated diene elastomer contain from 4 to 12 carbon atoms per molecule, preferably from 4 to 8.

Examples of these monomers are: 1,3-butadiene, chloroprene, isoprene, 2,3-dimethyl-1,3-butadiene and the relative mixtures. Isoprene and 1,3-butadiene are preferred, 1,3-butadiene is even more preferred.

The weight ratio between vinylarene and conjugated diene is from 10/90 to 40/60.

The preferred monovinylarene - conjugated di ne elastomer is the statistic styrene-butadiene copolymer (SBR).

The monovinylarene-conjugated diene elastomer can be produced according to the well known living anionic polymerization technique, using organic compounds of alkaline metals in an inert solvent as initiators. Typical inert solvents are pentane, hexane, cyclohexane, benzene, etc.; cyclohexane/hexane mixtures are preferable.

The molecular weight of the above statistic monovinylarene-diene elastomer is between 100,000 and 1,000,000, preferably between 200,000 and 500,000. The Mooney viscosity (ML_{1+4} at 100°C) is between 20 and 150,

lower viscosities giving insufficient wear resistance and higher viscosities causing processability problems.

As polymerization initiators of the conjugated diene or its copolymerization with the monovinylarene, n-butyl Lithium, sec-butyl Lithium, t-butyl Lithium, 1,4-dilithium butane, the reaction product of butyllithium and divinylbenzene, dilithiumalkylene, phenyl lithium, dilithium stilbene, diisopropenyl benzene dilithium, sodium naphthalene, lithium naphthalene, etc., can be used.

In the case of copolymerization, a Lewis base can be used as randomizing agent and regulator of the microstructure of the diene in the copolymer. Typical examples of the above Lewis bases are ethers and tertiary amines, for example dimethoxybenzene, tetrahydrofuran, dimethoxyethane, diethyleneglycoldibutylether, diethyleneglycoldimethylether, triethylamine, pyridine, N-methyl morpholine, N,N,N',N'-tetramethylethylenediamine, 1,2-diperidine ethane.

The content of monovinylarene linked to the polymer is controlled by the quantity of monomer present in the initial mixture, whereas the statistic distribution of the monovinylarene is obained by action of the Lewis base mentioned above, and it is preferable

for sequences of monovinylarene containing 10 or more units, to be less than 10% of the weight of the total monovinylarene.

When 1,3-butadiene is used, the content of 1,2 units of butadiene in the copolymer can be controlled by varying the polymerization temperature. In any case the content of vinyl in the copolymer, with reference to the butadiene part, must be within the range of 10 to 70%.

The living polymer can be produced by feeding the monomers, organic solvent, initiator based on organometallic compounds of an alkaline metal, and, if necessary, the Lewis base, into the reactor, in an inert atmosphere. The addition can be carried out in continuous or batch.

The polymerization temperature is usually between -120°C and +150°C, preferably between -80°C and +120°C, and the polymerization time is between 5 minutes and 24 hours, preferably between 10 minutes and 10 hours.

The temperature can be maintained at a constant value within the range indicated or it can be increased by means of a thermostating fluid or the reaction can be carried out under adiabatic conditions and the polymerization process can be in continuous or batch.

The concentration of the monomers in the solvent

is usually from 5 to 50% by weight, preferably from 10 to 35% by weight.

In the formation of the living polymer, it is necessary to prevent the presence of deactivating compounds, for example halogenated compounds, oxygen, water, carbon dioxide.

At the end of the polymerization, the reaction mixture is treated with polyfunctional coupling agents such as diphenyl or dialkyl carbonates, divinylbenzene, polyfunctional derivatives of Silicon (for example $SiCl_4$, trichloromethylsilane, trichlorophenylsilane), preferably with diphenyl or dialkyl carbonates.

Extinguishing agents such as water, alcohols and generally substances having labile hydrogens can also be used.

The above SBR elastomer preferably has a content of linked styrene of between 15 and 40% by weight, preferably between 20 and 30% by weight.

According to the present invention, the elastomeric mixture (a) must contain at least 20% by weight, preferably at least 40% by weight, of monovinylarene conjugated diene elastomer, preferably of statistic styrene butadiene copolymer (SBR).

As specified above, other elastomers can form part of the elastomeric mixture (a). Among these polybuta-

diene, obtained by polymerization in solution with catalysts of the Ziegler-Natta type or with Lithium catalysts, can be used, the polybutadiene having a vinyl content of between 0.5 and 80%.

In another embodiment of the present invention, the elastomeric mixture (a) consists of from 20 to 50% by weight, preferably from 30 to 40% by weight, of polybutadiene and from 50 to 80%, preferably from 60 to 70% by weight, of statistic styrene-butadiene copolymer having a content of epoxides of between 0.7 and 8.0%.

As well as polybutadiene, other elastomers selected from natural rubber and diene homo- or copolymers can form part of the elastomeric mixture (a). Among the latter it is convenient to mention poly 1,4 cis isoprene, styrene butadiene copolymer polymerized in emulsion, ethylene-propylene-diene terpolymer, chloroprene, butadiene-acrylonitrile copolymer.

With respect to the content of epoxide in the elastomeric mixture (a), this must be between 0.7 and 8%, preferably between 1.5 and 6.0%.

A lower quantity does not show significant advantages, whereas a higher percentage gives vulcanized products poor tensile properties. Moreover a percentage of epoxide higher than that specified leads to an increase in the glass transition temperature of the

polymer and therefore its use in tyre compounds will be critical.

The epoxy groups can be contained in any elastomer which forms part of the elastomeric mixture, but it is preferably contained in the monovinylarene-conjugated diene elastomer, even more preferably in the statistic butadiene styrene copolymer (SBR).

The methods for epoxidizing these elastomers are well known to experts in the field; for example the preparation of epoxidated SBR is described in US-A-4.341.672 and in Schulz, Rubber Chemistry & Technology, 55, 809 (1982).

The quantity of silica contained in the elastomeric composition is from 10 to 150 parts, preferably from 10 to 80 parts, even more preferably from 30 to 60 parts, per 100 parts of elastomeric material (a). When the content of silica is less than 10 parts, the reinforcing effect is insufficient and the wear resistance is poor; on the other hand when it exceeds 150 parts by weight, the processability and tensile properties are poor. In the preferred embodiment, the silica has a BET surface of between 100 and 250 m^2/g, a CTAB surface of between 100 and 250 m^2/g and an oil absorption (DBP) of between 150 and 250 ml/100 g (see EP-A-157.703 for the determination of these measure-

ments).

In addition 0-150 parts of carbon black, preferably from 2 to 50, even more preferably from 3 to 30, can be used as reinforcing charge together with the silica.

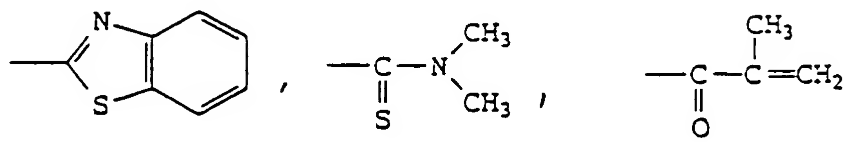
The composition consisting of (a) + (b) + (c) can be vulcanized with the usual techniques well known to experts in the field, i.e. with sulfur and/or sulfur donors and accelerating systems (for example zinc oxide, stearic acid and accelerators).

The vulcanized products thus obtained have a better wet grip and an improved hysteresis, as well as good tensile properties and a good wear resistance. These properties make the above vulcanized products suitable for use as treads for tyres.

The composition consisting of (a) + (b) + (c) can also be vulcanized in the presence, in addition to sulfur and/or sulfur donors, of silanes hereunder described.

A further object of the present invention therefore relates to an elastomeric composition for the production of treads for tyres which comprises, in addition to components (a) to (c) specified above, from 0.2 to 15 phr, preferably from 2 to 6 phr, of a silane having general formula (I) $Y_3\text{-Si-}C_nH_{2n}A$, wherein Y is an

alkoxide group having from 1 to 4 carbon atoms or a chlorine atom, n is an integer from 1 to 6; A is selected from $-S_mC_nH_{2n}Si-Y_3$, -X and SmZ, wherein X is selected from a nitrous, mercapto, amino, epoxy, vinyl, imide, chlorine group, Z is selected from



m is an integer from 1 to 6, Y is as defined above.

The addition of the component having general formula (I) allows an improved processability of the mixtures, even if the vulcanized product often has properties similar to those of the vulcanized product without the chemicals having general formula (I).

Typical examples of the above silanes having general formula (I) are:

bis(3-triethoxysilylpropyl)tetrasulfide,

bis(2-triethoxysilylethyl)tetrasulfide,

bis(3-trimethoxypropyl)tetrasulfide,

bis(2-trimethoxysilylethyl)tetrasulfide,

3-mercaptopropyltrimethoxysilane,

3-mercaptopropyltriethoxysilane,

2-mercaptoethyltrimethoxysilane,

2-mercaptoethyltriethoxysilane,

3-nitropropyltrimethoxysilane,

3-nitropropyltriethoxysilane, 3-choropropyltrimethoxysilane, 3-chloropropyl triethoxysilare, 2-chloroethyltriethoxysilane, 3-trimethoxysilylpropyl-N,N-dimethylthiocarbamoyltetrasulfide, 3-trimethoxysilylpropylbenzothiazoletetrasulfide, 3-triethoxysilylpropylmethacrylatemonosulfide, etc.

Among the above components bis(3-triethoxysilylpropyl)tetrasulfide, 3-trimethoxysilylpropylbenzothiazoletetrasulfide are preferred.

Among the components having general formula (I) wherein three different Ys are present, the following should be remembered: bis(3-diethoxymethylsilylpropyl)tetrasulfide 3-mercaptopropyldimethoxymethylsilane, 3-nitropropyldimethoxymethylsilane, 3-chloropropyldimethoxymethylsilane, dimethoxymethylsilylpropyl-N,N-dimethylthiocarbamoyltetrasulfide, dimethoxymethylsilylpropylbenzothiazoletetrasulfide.

When desired, the above elastomeric composition of the present invention can additionally contain antioxidants, antiozonants, plasticizers, "processing aids", as well as fillers in the form of powders, such as calcium carbonate, silicates, fibrous fillers such as glass fibre, carbon fibres etc.

The mixtures are prepared preferably using internal mixers, for example of the Banbury type.

It is also preferable to use two-step mixing cycles, the second of which for the addition of the vulcanizing system, optimized to obtain discharging temperatures of between 130 and 170°C, preferably between 140 and 160°C.

The vulcanization temperature is from 130 to 180°C, preferably from 140 to 170°C.

The following examples provide a better illustration of the present invention.

EXAMPLES

The copolymerization reaction is carried out according to the living polymerization technique according to what is described, for example, by M. Morton in "Anionic Polymerization, Principles and Practice" (Academic Press, New York, 1983).

As far as the epoxidation is concerned, the method of formation of peracid in situ is used, i.e. by directly reacting hydrogen peroxide as oxidant in the presence of a solution of an aliphatic acid, for example formic acid and acetic acid, and the polymeric substrate.

To maximize the yield of epoxide and minimize the opening of the epoxy ring previously formed (hydroxyla-

tion reactions), it is preferable not to use drastic temperatures and conditions.

The yield of epoxide is obtained by N.M.R. analyses carried out on the epoxidated polymer after coagulation and drying. The polymer thus isolated is dissolved in $CDCl_3$ and ^1H-NMR and ^{13}C-NMR scanning is carried out on the above polymeric solution; the ratio between the absorption of the protons relating to the species -CH-CH- at 2.8 ppm (with relation to the

$$\underset{\diagdown\;\diagup \atop \mathrm{O}}{\text{-CH-CH-}}$$

internal standard Me_4Si) and the olefinic ones determines the epoxidation reaction yield (see Pinazzi et al., Bull. Soc. Chem. Franc., 1973, Vol.59, page 1652. or R.V.Gemner and M.A.Golub, J. Pol. Soc., Polymer Chem. Ed. 1978, Vol. 16, page 2985).

The attribution of the percentage of epoxy groups linked to the polymeric chain is confirmed by the presence in the ^{13}C-NMR spectrum of signals at about 50 ppm (with relation to the internal standard Me_4Si) characteristic of the species -CH-CH-.

$$\underset{\diagdown\;\diagup \atop \mathrm{O}}{\text{-CH-CH-}}$$

EXAMPLE 1 - Preparation and vulcanization of Styrene-Butadiene copolymers defined with the initials A1, A2 and A3.

8000 grams of an anhydrous cyclohexane/hexane

mixture in a ratio of 9/1 by weight, 64 grams of THF and subsequently 250 grams of Styrene and 750 grams of Butadiene are feed into a stirred 20 litre reactor.

The temperature of the mass is brought to 40°C and 0.64 grams of Lithium n-butyl in cyclohexane are then fed. The beginning of the copolymerization is marked by the increase in temperature; when the maximum of about 80°C has been reached, the solution is left under stirring for 5 minutes; 0.6 grams of diphenylcarbonate in a solution of hexane are then added and the mixture is left under stirring for a further 10 minutes until the coupling reaction of the living chains is completed.

An aliquot (A2, 2,000 grams) of the polymeric solution is transferred to another reactor where it is subjected to epoxidation reaction by the addition of formic acid and hydrogen peroxide with a molar ratio with respect to the double bonds of 15/15/100.

The polymeric solution, to which 21 grams of formic acid have been added, is brought to a temperature of 70°C and 58.6 grams of hydrogen peroxide (30% w/w) are added dropwise over a period of 5 to 30 minutes.

At the end of the addition, the solution is maintained at about 70°C for a time of from 1 to 5 hours.

The epoxidation reaction is completed totally

eliminating both the water and the formic acid.

Sodium acetate or sodium bicarbonate is then added in a sufficient quantity to bring the pH to about 7.

2.9 grams of formic acid is added to a second aliquot (A3, 2,000 grams) of the polymeric solution and the temperature is brought to about 70°C. 8.0 grams of hydrogen peroxide (at 30% by weight) are added and the same procedure is adopted as described above.

0.3 phr of BHT (2,6-diterbutyl phenol) are added to the polymeric solutions A1 (this initial refers to the styrene-butadiene copolymer as such), A2 and A3, the mixture is coagulated with isopropyl alcohol and the coagulate is dried in an oven at 60°C for 4 hours.

The characteristics of the polymers A1, A2 and A3 are shown in Table 1, where % Epox. refers to the molar % of epoxidated double bonds with respect to the moles of initial diene double bonds.

GPC analyses of the partially epoxidated polymers A2 and A3 give molecular weight distributions similar to those obtained from the non-epoxidated polymer A1.

Owing to the low content of epoxy groups, th sample A3 does not form part of the present invention and is provided, together with the relative mixture M1-A3, for comparative purposes.

TABLE 1

Copolymer	A1	A2	A3
Styrene %	25.1	25.0	25.0
Vinyl %	47.2	50.2	50.3
<Mw>	259,300	254,300	n.d.
<Mn>	209,000	211,000	n.d.
Tg	-35°C	-29°C	-35°C
% Epox.	0	5	0.68
ML_{1-4} 100°C	58	67	54

Silica, carbon black, vulcanizing agents and other conventional additives were added to the control sample (A1) and the two copolymers A2 and A3, using a typical tread formulation, provided hereunder.

Styrene butadiene copolymer (SSBR) 100 parts, Cumarone resin 2 phr, Silica VN3 53 phr, Carbon black N330 4.25 phr, bis[3-triethoxysilylpropyl]tetrasulfide (Si69) 4.25 phr, ZnO 2.5 phr, Stearic acid 1.0 phr, Antioxidant 1.0 phr, Microcrystalline wax 1.0 phr, Aromatic oil 6.0 phr, CBS (N-cyclohexyl benzothiazolesulfeneamide) 1 phr, DPG (diphenylguanidine) 1.5 phr, sulfur 1.8 phr.

The compounds were produced using an internal Banbury type laboratory mixer and two-step mixing

cycles: the first, for incorporating the charges and Si69, was carried out in a Banbury mixer operating so as to obtain discharge temperatures of between 140 and 160°C; the second, for the addition of the vulcanizing system, was carried out in an open mixer; the total mixing time being 9 minutes.

The test-samples for the determination of the mechanical, dynamic and dynamomechanical properties were vulcanized in a press at 151°C for 60 minutes.

The properties of the vulcanized products are shown in table 2. The tanδ measurements are particularly significant. In fact, it is generally known that the tanδ measurement at a temperature of about 60-80°C and strain of between 2 and 5% is indicative of the rolling resistance of the vulcanized mixture, whereas tanδ at about 0°C and low strains (about 0.1%) can instead be correlated with the wet grip.

TABLE 2

Compound	M1-A1	M1-A2	M1-A3
100% Modulus (MPa)	4.5	5.3	4.4
200% Modulus (MPa)	8.9	11.3	9.3
Tensile strength (MPa)	16.3	17.5	18.3
Elongation at break (%)	332	282	349
Hardness (Shore A)	78	75	77
Abrasion loss (mm^3)	136	111	125
tanδ 1Hz, 0.1% strain, 0°C	0.127	0.247	0.126
tanδ 1Hz, 5% strain, 60°C	0.138	0.097	0.142
tanδ 1Hz, 10% strain, 60°C	0.155	0.102	0.153

As can be seen from the data of table 2, the epoxidated copolymer A2 (see compound M1-A2) produces a better interaction with the silica compared to the corresponding non-epoxidated copolymer.

The improvement in the interaction between rubber and filler is shown by the improvement in the abrasion resistance and dynamic properties.

In particular the variation of tanδ with temperature and strain is significant and indicates an improvement in wet grip and in rolling resistance (lower hysteresis).

With respect to the degree of epoxidation useful

to obtain an improvement in dynamic properties, it can be noted how the properties of the compound M1-A3 are not significantly different from those of the compound without epoxy groups.

EXAMPLE 2 - Preparation and vulcanization of Styrene-Butadiene copolymers A4 and A5.

Using a procedure similar to that described in example 1, two styrene-butadiene copolymers are prepared, one non-epoxidated called A4 and the other epoxidated called A5 and derived from the first one.

The two copolymers A4 and A5 have the properties listed in table 3.

TABLE 3

Copolymer	A4	A5
Styrene %	25.1	24.9
Vinyl %	63.5	64.9
<Mw>	246,800	239,400
<Mn>	191,000	180,000
Tg	-21°C	-20°C
% Epox.	0	2.27
ML_{1-4} 100°C	53	53

According to the procedure described in example 1, another two compounds are prepared with the two poly-

mers, M1-A4 with the non-epoxidated copolymer A4 and M1-A5 with the partially epoxidated copolymer A5.

The two compounds are vulcanized according to the procedure described above. The properties of the vulcanized products are shown in table 4.

TABLE 4

Compound	M1-A4	M1-A5
100% Modulus (MPa)	4.2	4.4
200% Modulus (MPa)	10.2	11.2
Tensile strength (MPa)	17.0	17.5
Elongation at break (%)	294	282
Hardness (Shore A)	73	72
Abrasion loss (mm^3)	153	146
tanδ 1Hz, 0.1% strain, 0°C	0.432	0.648
tanδ 1Hz, 5% strain, 80°C	0.079	0.077
tanδ 110 Hz, 6% strain, 80°C	0.132	0.125

From the data of table 4 it can be seen that the epoxidated copolymer A5 (compound M1-A5) has improved hysteretic properties (lower tanδ at high frequency conditions, high temperature and strain). In addition the compound has an improved wet grip as shown by the tan δ value at 0°C.

EXAMPLE 3

The copolymers A1 and A2 described in example 1 are fcrmulated with silica and additives, but without mercaptosilane (compounds M2-A1 and M2-A2); the formu-lations are shown in table 5 where, for comparative pur-poses, the previous compound M1-A2 obtained from epoxidated copolymer A2 but in the presence of mercap-tosilane, is also indicated. In this table the bis[3-triethoxysilylpropyl] tetrasulfide is abbreviated as Si69.

TABLE 5

Compound Component	M1-A2 (phr)	M2-A1 (phr)	M2-A2 (phr)
SSBR	100.0	100.0	100.0
Coumarone resin	2.0	2.0	2.0
Silica VN3	53.0	53.0	53.0
Carbon black N330	4.25	4.25	4.25
Si69	4.25	0.00	0.00
Zno	2.5	2.5	2.5
Stearic acid	1.0	1.0	1.0
Antioxidant	1.5	1.5	1.5
Wax	1.0	1.0	1
Aromatic oil	6.0	6.0	6.0
CBS	1.0	1.0	1.0
DPG	1.5	1.5	1.5
Sulfur	1.8	1.8	1.8
TOTAL PHR	179.8	175.55	175.55

The formulations indicated in table 5 are then subjected to vulcanization under the conditions described in example 1.

The properties of the vulcanized products are shown in table 6.

TABLE 6

Compound	M1-A2	M2-A1	M2-A2
100% Modulus (MPa)	5.3	2.4	4.3
200% Modulus (MPa)	11.3	4.3	10.0
Tensile strength (MPa)	17.5	18.4	15.0
Elongation at break (%)	282	634	310
Hardness (Shore A)	75	74	74
Abrasion loss (mm^3)	111	179	127
tanδ 1Hz, 0.1% strain, 0°C	0.247	0.109	0.250
tanδ 1Hz, 5% strain, 60°C	0.097	0.157	0.092

It is evident from the data of table 6 that, even without the addition in the formulation of a compatibilizing agent (i.e of the silane in situ modifier of the silica), the epoxidated copolymer A2 has an improved abrasion resistance and hysteresis, the latter similar to that obtained with the compound vulcanized with silane.

EXAMPLE 4 - Preparation and vulcanization of the

styrene-butadiene copolymers called A6, A7 and A8.

Using a procedure similar to that described in example 1, three styrene-butadiene copolymers are prepared, whose characteristics are shown in table 7.

TABLE 7

Copolymer	A6	A7	A8
Styrene %	19.9	19.4	20.4
Vinyl %	67.3	71.1	74.3
<Mw>	n.d.	n.d.	n.d.
<Mn>	n.d.	n.d.	n.d.
Tg	-24°C	-19°C	-15°C
% Epox.	0	3.63	6.3
ML_{1-4} 100°C	52	54	70

The above copolymers has been compounded with and without mercaptosilanes according to the formulations indicated in table 8.

TABLE 8

Compound Component	M1(A6-A7-A8) (phr)	M2(A6-A7-A8) (phr)
SSBR	100.0	100.0
Coumarone resin	2.0	2.0
Silica VN3	53.0	53.0
Carbon black N330	4.25	4.25
Si69	4.25	0.00
Zno	2.5	2.5
Stearic acid	1.0	1.0
Antioxidant	1.5	1.5
Wax	1.0	1.0
Aromatic oil	6.0	6.0
CBS	1.0	1.0
DPG	1.5	1.5
Sulfur	1.8	1.8
TOTAL PHR	179.8	175.55

The formulations of table 8 were vulcanized under the conditions described in example 1.

The properties of the vulcanized products are indicated in table 9.

TABLE 9

Compound	M1-A6	M2-A6	M1-A7	M2-A7	M1-A8	M2-A8
Mooney visc.	68	121	84	131	95	118
100% Modulus	3.0	2.1	3.3	2.8	3.1	3.3
300% Modulus	13.5	6.7	--	10.8	--	--
Tensile stren.	17.6	17.9	15.5	19.0	17.7	16.9
Elong. at break	366	606	286	467	277	283
Hardness	69	70	70	71	72	72
Abrasion loss	138	191	134	160	128	127

From the data of table 9 it can again be observed how the epoxidation is in itself capable of improving the polymer-silica interaction, as shown by the improvement in the abrasion resistance without mercaptosilane.

The addition of mercaptosilane however has the effect of improving the processability, as shown by the Mooney viscosity of the compound.

EXAMPLE 5 - Vulcanization of mixtures with polybutadiene.

Silica and conventional additives, except for mercapto-silane (abbreviated Si69), are added to the comparative copolymers A1 and A4 and the partially epoxidated copolymers A2 and A5 with polybutadiene,

according to the formulations indicated in table 10.

TABLE 10

Compound Component	M3-A1 (phr)	M3-A2 (phr)	M3-A4 (phr)	M3-A5 (phr)
SSBR	65.0	65.0	65.0	65.0
Polybut. high cis	35.0	35.0	35.0	35.0
Coumarone resin	2.0	2.0	2.0	2.0
Silica VN3	53.0	53.0	53.0	53.0
Carbon black N330	4.25	4.25	4.25	4.25
Si69	0.0	0.0	0.0	0.0
ZnO	2.5	2.5	2.5	2.5
Stearic acid	1.0	1.0	1.0	1.0
Antioxidant	1.5	1.5	1.5	1.5
Wax	1.0	1.0	1.0	1.0
Aromatic oil	6.0	6.0	6.0	6.0
CBS	1.0	1.0	1.0	1.0
DPG	1.5	1.5	1.5	1.5
Sulfur	1.8	1.8	1.8	1.8
TOTAL PHR	175.55	175.55	175.55	175.55

After vulcanization under the conditions indicated above, vulcanized products are obtained whose properties are shown in Table 11.

TABLE 11

Compound	M3-A1	M3-A2	M3-A4	M3-A5
Mooney viscosity	140	141	139	136
100% Modulus (MPa)	2.0	3.6	2.0	2.9
300% Modulus (MPa)	4.7	12.9	5.0	9.1
Tensile strength (MPa)	17.8	14.2	17.7	18.3
Elongation at break (%)	772	323	732	520
Hardness (Shore A)	75	77	74	77
Abrasion loss (mm^3)	119	43	119	90
tanδ 1Hz, 0.1% strain, 0°C	0.099	0.147	0.120	0.137
tanδ 1Hz, 5% strain, 60°C	0.149	0.142	0.153	0.145

From the data of table 11 it is evident that the two partially epoxidated polymers (A2 and A5), even without silane as a compatibilizing agent, produce compounds with a good interaction with silica, especially in blends containing polybutadiene.

Consequently the rolling resistance (lower hysteresis), abrasion resistance and wet grip are improved.